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## Hardness of CaF<sub>2</sub> and BaF<sub>2</sub> Solid Lubricants at 25 to 670 °C

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## HARDNESS OF $\text{CaF}_2$ AND $\text{BaF}_2$ SOLID LUBRICANTS AT 25 TO 670 °C

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### SUMMARY

Plastic deformation is a prominent factor in determining the lubricating value of solid lubricants. Little information is available and its direct measurement is difficult so hardness, which is an indirect measure of this property was determined for fluoride solid lubricant compositions.

The Vickers hardness of  $\text{BaF}_2$  and  $\text{CaF}_2$  single crystals was measured up to 670 °C in a vacuum. The orientation of the  $\text{BaF}_2$  was near the (013) plane and the  $\text{CaF}_2$  was about 16° from the (111) plane.  $\text{BaF}_2$  has a hardness of 83 kg/mm<sup>2</sup> at 25 °C and 9 at 600 °C and  $\text{CaF}_2$  is 170 at 25 °C and 13 at 670 °C. The decrease in hardness in the temperature range of 25 to 100 °C is very rapid and amounts to 40 percent for both materials.

Melts of  $\text{BaF}_2$  and  $\text{CaF}_2$  were made in a platinum crucible in ambient air with compositions of 50 to 100 wt %  $\text{BaF}_2$ . The Vickers hardness of these polycrystalline binary compositions at 25 °C increased with increasing  $\text{CaF}_2$  reaching a maximum of 150 kg/mm<sup>2</sup> near the eutectic. The polycrystalline  $\text{CaF}_2$  was 15 percent softer than that of the single crystal surface and  $\text{BaF}_2$  was 30 percent harder than the single crystal surface. The microstructure of these melts was that of rounded grains of  $\text{CaF}_2$  dispersed in a fine  $\text{BaF}_2$  matrix. Some small, but undetermined amount of solid solution of  $\text{CaF}_2$  in the  $\text{BaF}_2$  was found.

A melt of 62 wt %  $\text{BaF}_2$  - 38 wt %  $\text{CaF}_2$  was made in a nickel crucible in a nitrogen atmosphere. It was found to be 30 percent harder than the melts made in a platinum crucible in air.

It is estimated that the brittle to ductile transition temperature for  $\text{CaF}_2$  and  $\text{BaF}_2$  is <100 °C for the conditions present in the hardness tester.

### INTRODUCTION

There is a great need in current technology for solid-lubricated systems that will perform satisfactorily over a wide range of temperatures. For example, the achievement of major advances in high-temperature lubrication are essential for the development of more fuel-efficient engines such as the adiabatic diesel and advanced turbomachinery (ref. 1). Other examples are the advanced Sterling engine and numerous aerospace mechanisms. Maximum temperatures of 600 to 1100 °C are anticipated for critical sliding contacts in these applications (refs. 2 to 5).

Solid lubricant materials that are thermally and chemically stable (non-reactive) at the temperature quoted include certain soft oxides, vitreous glazes, fluorides of the alkaline earth metals, and soft noble metals such as gold and silver.

The mechanism of lubrication with these materials requires first of all that they adhere to the surfaces to be lubricated. They must also exhibit a high degree of plasticity so that they flow rather than fragment within the sliding contact. In other words, a solid lubricant must be a ductile material with a low yield strength in the shear direction.

For ductile materials, yield strength is directly proportional to the indentation hardness divided by three (ref. 6). For ionic crystals the yield strength is proportional to the hardness divided by 35 (ref. 6). Therefore, hot hardness measurements should give considerable insight concerning the influence of temperature on the plastic flow properties of candidate solid lubricant materials. If a material is brittle at lower temperatures, but undergoes a brittle to ductile transition at some higher temperature, hot hardness measurements should be helpful in identifying the transition temperature.

In many materials the brittle to ductile transition temperature is strain rate dependent. The mechanical properties of  $\text{CaF}_2$  and  $\text{BaF}_2$  single crystals have been studied by others to gain knowledge about fluorite type ionic solids (refs. 7 to 10). Compressive, tensile, and bending studies have provided some very limited information about the plasticity and strain rate dependence of the brittle to ductile transition temperature.

Parker (ref. 7) reported that  $\text{CaF}_2$  showed no ductility in room temperature bend tests. Phillips (ref. 8) studied the deformation and fracture of  $\text{CaF}_2$  and found no ductility in compression tests at temperatures below 400 °C at a strain rate of  $6 \times 10^{-2}$ /min. Burn (ref. 9) in three point bending tests on  $\text{CaF}_2$  found considerable plastic flow before fracture at 175 °C using a strain rate of  $10^{-4}$ /min. In fact the specimens would creep to fracture if the load was maintained constant shortly after yielding was detected. Liu (ref. 10) found plastic flow in compression tests of  $\text{BaF}_2$  at <175 °C for an initial strain rate of  $6 \times 10^{-3}$ /min. This information indicates that the brittle to ductile transition temperature of these fluorides is very strain rate sensitive. This implies that the hardness of these materials at a particular temperature will be dependent on the strain rate of the hardness tester.

Coatings containing chemically stable  $\text{CaF}_2$  and  $\text{BaF}_2$  are known to lubricate at temperatures from about 400 to 1000 °C, but do not lubricate at lower temperatures (ref. 11). The improvement in lubricating ability at the higher temperatures can be attributed to: (a) the softening effect of increasing temperature, and (b) the onset of ductility above the brittle to ductile transition temperature. Hardness measurements as a function of temperature are instructive in explaining this behavior.

Low temperature friction of fluoride containing coatings has been improved by the addition of a small amount of a soft metal such as silver to the coating composition (ref. 12). Therefore, the scope of this paper includes not only hardness data for  $\text{CaF}_2$ ,  $\text{BaF}_2$ , and binary compositions of these two but also reference hardness data from a literature source for metallic silver (ref. 13).

Vickers hardness measurements of single crystal  $\text{CaF}_2$  and  $\text{BaF}_2$  were made from 25 to 670 °C. In addition, the hardness of polycrystalline  $\text{CaF}_2$ ,  $\text{BaF}_2$ , and binary compositions in the range of 50 to 90 wt %  $\text{BaF}_2$  were prepared and measured. This latter composition range covers the region of current interest in solid lubrication.

## EXPERIMENTAL

### Hardness Measurement

High temperature hardness measurements were made using a commercial test machine equipped with a vacuum chamber and pumping system, separate indenter and specimen furnaces with variable temperature set point controllers, an optical microscope indent measuring system, and an automatic indentation mechanism. A Vickers pyramidal diamond indenter was used. The diamond was attached by mechanical embedment in a high temperature tantalum alloy holder. This holder is threaded for attachment to the loading mechanism. The holder also contains a thermocouple well for temperature measurement and control of the indenter. A typical measurement was made as follows. The specimen in the form of a 5- by 5- by 10-mm bar was installed in the specimen furnace and the indenter in its furnace. The chamber was evacuated to a pressure of  $8 \times 10^{-5}$  to  $1 \times 10^{-4}$  torr. The indenter and specimen furnaces were heated to the maximum desired temperature and when this temperature was reached and controlling occurred for 10 to 15 min a series of five or more indents were made and the diagonals measured. The temperature set point was lowered on each furnace and when control was established for 5 to 10 min another set of indents was made. The hardness was determined for each set of indent diagonal measurements and the average hardness for all measurements was calculated and reported in units of  $\text{kg/mm}^2$ . The standard deviation for each hardness set was calculated. The temperature of the indenter was always kept within  $5^\circ\text{C}$  of the specimen. This was necessary to minimize the influence of the indenter temperature on the specimen temperature. An indenter travel rate of 0.5 mm/sec, a dwell time of 10 sec and a load of 50 g (0.5 N) was used.

Room temperature hardness measurements of the polycrystalline melt compositions were made on a different commercial machine usable only at room temperature in ambient air at atmospheric pressure. A Vickers indenter was used with a 50 g (0.5 N) load. The loading rate and dwell time were not controllable and their values were not known. Five or more indents were made and the hardness was determined from the measured diagonals. A standard deviation for the hardness set was calculated. It was found that the room temperature hardness of the same specimen measured on the high temperature machine was in good agreement with that made on this machine. For example, the hardness of the  $\text{BaF}_2$  single crystal was  $82 \pm 3$  on the high temperature machine and  $79 \pm 1$  on the room temperature machine. Similarly the hardness values for  $\text{CaF}_2$  were  $169 \pm 4$  and  $169 \pm 3$ , respectively.

### Single Crystal Materials

Single crystals of  $\text{CaF}_2$  and  $\text{BaF}_2$  in the form of random pieces with several polished faces were procured from a commercial source. The major impurities are Mg, Na, Si, and Fe with a total  $<0.1$  wt %. The crystals were cut into 5- by 5- by 10-mm bars preserving the as received polished face. These bars were given no further mechanical, thermal, or chemical treatment.

The crystal orientation of the polished face was determined by the standard Laue back reflection x-ray diffraction and data reduction methods (refs. 14 and 15). The normal to the polished face is shown on the unit stereographic triangle in the standard (001) projection in figure 1. For  $\text{CaF}_2$  the orientation of the polished hardness surface was about 16 degrees off the (111)

plane while the  $\text{BaF}_2$  orientation was near the (013) plane. Both of these materials have the fluorite cubic crystal structure. The lattice parameter of the  $\text{CaF}_2$  was 5.46 Å and the value for the  $\text{BaF}_2$  was 6.20.

### Polycrystalline Materials

The  $\text{CaF}_2$  and  $\text{BaF}_2$  starting materials for all melts were reagent grade powders. A spectrographic analysis of the starting materials and melts showed the impurities to be Fe, Mg, Na, and Si with a total of <0.15 wt % in every case. The Ni content of the melt made in a Ni crucible was <10 ppm.

Polycrystalline hardness specimens in the  $\text{CaF}_2$ - $\text{BaF}_2$  binary system were prepared by melting the reagent grade materials in a platinum crucible in ambient air at atmospheric pressure (Pt/air). The powders were weighed out to 0.1 g and mixed by shaking in a plastic bottle. An electrically heated furnace was used. Typical heating schedules are presented in figure 2. The crucible was placed in the furnace at 800 to 850 °C, the temperature was raised to the liquidus or melting point temperature and held for 30 to 40 min at temperatures as high as 20 to 30 °C above the liquidus or melting point. The power to the furnace was shut off and the melt was furnace cooled to 700 to 750 °C where it was removed and air cooled to room temperature. The average furnace cooling rate over the first 10 to 15 min was 10 to 15 °C/min. The solidified melt was mechanically removed from the crucible as random sized pieces. One melt of 62 wt %  $\text{BaF}_2$  - 38 wt %  $\text{CaF}_2$  was made by melting in a nickel crucible in a nitrogen atmosphere ( $\text{Ni/N}_2$ ).

Several pieces of a solidified melt were mounted in plastic mounting material and diamond polished but not etched. Hardness measurements were made on the polished surface. This surface was also studied by optical and scanning electron microscopy (SEM) and energy dispersive x-ray (EDX) techniques. Before the SEM examination a sputtered gold coating about 100 Å thick was applied to minimize charging.

## RESULTS AND DISCUSSION

### Single Crystals

The Vickers hardness results for single crystals of  $\text{CaF}_2$  and  $\text{BaF}_2$  at temperatures of 25 to 670 °C are presented in figures 3 and 4 along with data for polycrystalline silver taken from reference 13. The orientation of the hardness test surfaces for the fluoride materials is given in figure 1. Both fluoride materials exhibit a rapid decrease in hardness at low temperatures. From 25 to 100 °C there is a hardness loss of 40 percent. At 600 °C the hardness of each is near 10 which is similar to silver at this temperature (ref. 13). For  $\text{CaF}_2$  there is a second rapid period of hardness change starting near 400 °C.

Hardness data for single crystal  $\text{CaF}_2$  on the (111) plane taken from reference 16 are included in figure 3 for reference purposes. These measurements were made using a Knoop indenter and the values are about 10 to 20 percent higher than the present values and exhibit a smaller temperature dependence in the 25 to 100 °C range. The hardness of  $\text{CaF}_2$  is anisotropic. Different orientations were used so different hardness values would be expected.

Figure 5 is a plot of hardness data versus dwell time for single crystal  $\text{CaF}_2$  at 22 and 250 °C taken from reference 16. This information indicates a large amount of indentation creep especially in the first 100 sec. This creep produces a time dependent hardness value. For example, at 22 °C the hardness is 165 kg/mm<sup>2</sup> with a dwell time of 30 sec and 148 at 100 sec.

Figures 6 and 7 are photomicrographs of the Vicker indents made at various temperatures. The photographs were made at room temperature. For  $\text{CaF}_2$  there are cracks emanating from the indents made at temperatures up to 85 °C while no such features are present above this temperature. Also the indents are slightly shorter on one side. This is due to the hardness anisotropy. The indents in the  $\text{BaF}_2$  show evidence of slip plane steps along the sides of the impressions at temperatures higher than 94 °C. This is caused by slip in the plastic zone immediately under the indenter (ref. 17). This latter feature is not present in the  $\text{CaF}_2$  indents. These observations suggest that both fluorides have a brittle to ductile transition temperature of less than 100 °C. The rapid rise in hardness at less than 100 °C confirms this conclusion.

### Brittle to Ductile Transition

It is known from a limited number of mechanical property measurements (refs. 7 to 10) that the brittle to ductile transition temperature of  $\text{CaF}_2$  and  $\text{BaF}_2$  is sensitive to strain rate. This is illustrated in plots 8(a) and 8(b). In figure 8(a) the two values for  $\text{CaF}_2$  (refs. 8 and 9) are plotted on a semi-log scale and connected by a straight line and a line was drawn through the single  $\text{BaF}_2$  point (ref. 10) parallel to the  $\text{CaF}_2$  line. This information indicates that the brittle to ductile transition temperature of  $\text{CaF}_2$  and probably  $\text{BaF}_2$  decreases rapidly with decreasing strain rate. Figure 8(b) was constructed on linear axis from the data in figure 8(a). This plot shows more clearly the relationship between the brittle to ductile transition temperature and strain rate. It can be inferred that the transition temperature of  $\text{CaF}_2$  asymptotically approaches 400 °C at high strain rates ( $10^{-1}$ ) and 300 °C for  $\text{BaF}_2$ .

This data is not inconsistent with the present estimate of the brittle to ductile transition of less than 100 °C if the strain rate produced by the hardness tester is low. From figure 8(b) the transition temperature can be estimated to be less than 100 °C for a strain rate in the range of  $10^{-4}$  to  $10^{-5}$ /min. The strain rate produced by the hardness tester could reasonably be in this range.

The large influence of strain rate on the brittle to ductile transition temperature of these materials may significantly influence their temperature range of solid lubrication. The ductile state provides better lubrication. Therefore, to achieve the best possible lubrication at low temperatures would require very low strain rates such as at startup or during low-speed sliding operation. This is an interesting area for further consideration and analysis.

It has been observed in sliding friction and wear tests that the temperature for onset of lubrication by these fluorides is >400 °C. This indicates a high strain rate to exist in the sliding friction and wear tests compared to that in the hardness tester.

## Polycrystalline Melts

When the fluorides are used as solid lubricants they are not single crystals but polycrystalline solids. Therefore information about the hardness of polycrystalline solids formed by melting was obtained.

Room temperature Vickers hardness of the solidified melts versus temperature are presented in figure 9(a). A tentative and incomplete binary phase diagram (ref. 18) is shown in figure 9(b) for ready reference. A peritectic is indicated at about 62 wt %  $\text{BaF}_2$  and a eutectic near 70 wt %. The eutectic temperature is 1050 °C and the peritectic temperature is 1070 °C. Some solid solution of  $\text{CaF}_2$  in the  $\text{BaF}_2$  is shown in the composition range on the  $\text{BaF}_2$  rich side of the eutectic. With increasing  $\text{CaF}_2$  there is a rapid increase in hardness up to about 40 wt %  $\text{CaF}_2$ . Compositions with greater than this amount of  $\text{CaF}_2$  show little or no further change in hardness.

The 62 wt %  $\text{BaF}_2$  melt made in  $\text{Ni/N}_2$  is about 30 percent harder than those of similar compositions melted in  $\text{Pt/air}$ . Also the polycrystalline  $\text{BaF}_2$  is 30 percent harder than the single crystal while the  $\text{CaF}_2$  melt is 15 percent softer than its single crystal. A difference can be expected because of the anisotropy of the single crystals and the hardness of polycrystalline materials is an average of the randomly oriented grains with probably contributions from grain boundary effects.

The microstructure of the binary melts is shown in figure 10. Melts up to the peritectic composition of 62 wt %  $\text{BaF}_2$  exhibit large, rounded, globular grains in a fine matrix. At the eutectic composition of 70 wt %  $\text{BaF}_2$  a fine laminar phase is present. For  $\text{BaF}_2$  contents above the eutectic many small round grains are present.

The composition of the microstructural features were identified by EDX examination. The results of this examination for the 60 wt %  $\text{BaF}_2$  - 40 wt %  $\text{CaF}_2$  composition are presented in figure 11. The large dark rounded grains are primarily  $\text{CaF}_2$  and the matrix is mainly  $\text{BaF}_2$ . This indicates that on cooling the melt the  $\text{CaF}_2$  precipitates as rounded grains in a matrix of  $\text{BaF}_2$ . EDX examinations of the 62 wt % (melted in  $\text{Ni/N}_2$ ) and the 80 wt %  $\text{BaF}_2$  compositions gave the same results, that is the dark rounded grains are  $\text{CaF}_2$  and the matrix is  $\text{BaF}_2$ .

It is interesting to note that the hardness of the large dark rounded grains in the 50, 60, and 62 wt %  $\text{BaF}_2$  compositions were within 5 percent of that at any other area on the surface.

An x-ray diffraction (XRD) examination of the melts and starting materials was made for the purpose of determining the components present and their lattice constants. From the lattice constants the presence of solid solution can be determined. The results are presented in table I and plotted in figure 12. The lattice parameters were determined by use of a  $\cos^2 \theta \cot \theta$  extrapolation function (ref. 19). This procedure reduces systematic errors involved in the measurements. The lattice parameter of the  $\text{BaF}_2$  before and after melting are close in value and agree well with the ASTM card no. 4-0452 (ref. 20). Both the melted and not melted  $\text{CaF}_2$  lattice parameters are larger than the ASTM card no. 4-0864 value (ref. 20). A small amount of  $\text{CaO}$  was found in the melted  $\text{CaF}_2$ .

The lattice parameter of the  $\text{BaF}_2$  in the binary melts made in the Pt/air condition shows a decrease as the  $\text{CaF}_2$  content rises. This decrease in the lattice parameter of the  $\text{BaF}_2$  suggests solid solubility of  $\text{CaF}_2$  in the  $\text{BaF}_2$  lattice. Other data (ref. 18) for this binary system tentatively indicates a small amount of solid solution of  $\text{CaF}_2$  in the  $\text{BaF}_2$ . The  $\text{BaF}_2$  parameter ceases to decrease at compositions containing >20 wt % of  $\text{CaF}_2$  which suggests that a maximum solubility is reached. This solution may contribute to the increased hardness with increased  $\text{CaF}_2$  content in the binary compositions at the high  $\text{BaF}_2$  end of the diagram.

$\text{CaF}_2$  is detected by XRD in all the binary melts. However, the patterns are not sharp and intense. It was not possible to determine the lattice parameter of the  $\text{CaF}_2$  from these patterns because the high angle lines which are needed for good extrapolation were either not present or if present were not sharply defined. It can be suggested that the poor patterns may be due to amorphous or less well developed  $\text{CaF}_2$  crystals. In the compositions of higher  $\text{BaF}_2$  content this may be due to the lower concentrations of  $\text{CaF}_2$  present. Examination of the few low angle lines present would indicate no change in the lattice parameter of the  $\text{CaF}_2$  in any of the binary compositions.

The lattice parameter of the  $\text{BaF}_2$  in the 62 wt %  $\text{BaF}_2$  - 38 wt %  $\text{CaF}_2$  composition melted in Ni/ $\text{N}_2$  was much smaller than that of similar compositions melted in Pt/air. This composition was 30 percent harder than the Pt/air melts of similar compositions. This leads to the conclusion that melting conditions such as container, atmosphere, and probably cooling rates (annealing) are important in determining hardness. Oxygen contamination of single crystal  $\text{CaF}_2$  has been shown to increase its hardness by 10 to 13 percent while nitrogen contamination caused no change (ref. 21).

## CONCLUSIONS

A study was made of the hardness-temperature characteristics of  $\text{BaF}_2$ ,  $\text{CaF}_2$ , binary mixtures of these fluorides and silver to determine whether these characteristics are related to the temperature range over which these materials are effective as dry film lubricants. The major observations in this study were the following:

1. The hardness of single crystal  $\text{CaF}_2$  and  $\text{BaF}_2$  decreases rapidly with a loss of about 40 percent between 25 and 100 °C. The Vickers hardness values of the fluorides and silver are between 10 and 30 kg/mm<sup>2</sup> over the temperature range at which these materials are known to be effective solid lubricants. That is from below room temperature to about 550 °C for silver, and from about 450 to above 900 °C for the fluorides.

2. From observations of the nature of the indents and the rapid decrease in hardness with temperature it is estimated that the brittle to ductile transition temperature for the fluorides is in the 25 to 100 °C range at low-strain rates. Literature data shows this transition is strain rate sensitive and confirms our results for a strain rate during the hardness indentation in the range of  $10^{-4}$  to  $10^{-5}$ /min.

3. The hardness of polycrystalline binary compositions of  $\text{CaF}_2$  and  $\text{BaF}_2$  at 25 °C increases with increasing  $\text{CaF}_2$  reaching a maximum of about 150 kg/mm<sup>2</sup>



near 60 wt % BaF<sub>2</sub>. Polycrystalline CaF<sub>2</sub> was 15 percent softer than the single crystal surface and the BaF<sub>2</sub> was 30 percent harder.

4. The microstructure of the polycrystalline binary compositions is that of rounded grains of CaF<sub>2</sub> in a matrix of BaF<sub>2</sub>. In the composition range of 50 to 90 wt % BaF<sub>2</sub> the CaF<sub>2</sub> grains become progressively smaller as the BaF<sub>2</sub> increases. At the peritectic composition a laminar structure is present. There is some solid solution of CaF<sub>2</sub> in the BaF<sub>2</sub> lattice.

5. The hardness of the binary polycrystalline compositions is influenced by the method of preparation.

#### REFERENCES

1. Pinkus, O.; and Wilcock, D.F.: Strategy for Energy Conservation Through Tribology, ASME, 1977.
2. Kamo, R.; and Bryzik, W.: Cummins/IACOM Advanced Adiabatic Engine, Proceedings of the Twenty-First Automotive Technology Development Contractors' Coordination Meeting, SAE P-138, SAE, 1984, pp. 121-134.
3. Groseclose, L.E.; Helms, H.E.; and Johnson, R.A.: AGI 100 Advanced Gas Turbine Technology Project. Proceedings of the Twenty-First Automotive Technology Development Contractors' Coordination Meeting, SAE P-138, SAE, 1984, pp. 263-272.
4. Kreiner, D.M.; and Kidwell, J.R.: AGI 100 Advanced Gas Turbine Technology Project. Proceedings of the Twenty-First Automotive Technology Development Contractors' Coordination Meeting, SAE P-138, SAE, 1984, pp. 273-285.
5. Litran, R.H.; and Stephens, J.R.: Advanced High Temperature Materials for the Energy Efficient Automotive Stirling Engine. NASA TM-83659, 1984.
6. Peterson, M.B.; and Winer, W.O., eds.: Wear Control Handbook, ASME, 1980, p. 1320.
7. Parker, E.R., et al.: Ductile Ceramics - A High Temperature Possibility. J. Met., vol. 10, no. 5, May 1958, pp. 351-353.
8. Phillips, W.L., Jr.: Deformation and Fracture Processes in Calcium Fluoride Single Crystals. J. Am. Ceram. Soc., vol. 44, no. 10, Oct. 1961, pp. 499-506.
9. Burn, R.A.; and Murray, G.T.: Plasticity and Dislocation Etch Pits in CaF<sub>2</sub>. J. Am. Ceram. Soc., vol. 45, no. 5, Nov. 1964, pp. 251-252.
10. Liu, T.S.; and Li, C.H.: Plasticity of Barium Fluoride Single Crystals. J. Appl. Phys., vol. 35, no. 11, Nov. 1964, pp. 3325-3330.
11. Sliney, H.E.: Wide Temperature Spectrum Self-Lubricating Coatings Prepared by Plasma Spraying, Thin Solid Films, vol. 64, pp. 211-217, 1979.

12. Sliney, H.E.: The Use of Silver in Self-Lubricating Coatings for Extreme Temperatures. ASLE Trans., vol 29, no. 3, July 1986, pp. 370-376.
13. Lozinskii, M.G.: High Temperature Metallography, Pergamon Press, 1961, p. 355.
14. Cullity, B.D.: Elements of X-Ray Diffraction, Addison-Wesley, 1949, p. 224.
15. Wood, E.A.: Crystal Orientation Manual, Columbia Univ. Press, 1963, p. 32.
16. O'Neil, J.B.; Redfern, B.A.W.; and Brookes, C.A.: Anisotropy in the Hardness and Friction of Calcium Fluoride Crystals. J. Mater. Sci., vol. 8, no. 1, Jan. 1973, pp. 47-58.
17. Evans, A.G., ed.: Fracture in Ceramic Materials - Toughening Mechanisms, Machining Damage and Shock. Noyes Publications, 1984, pp. 283-304.
18. Levin, E.M.; and McMurdie, H.F.: Phase Diagrams for Ceramists, 1975 Supplement, M.K. Reser, Ed., American Ceramic Society, Diagram No. 4813, 1975, p. 358.
19. Azaroff, L.V.; and Buerger, M.J.: The Powder Method in X-Ray Crystallography. McGraw-Hill Co., 1958, p. 235.
20. Smith, J.V., ed.: X-Ray Powder Data File, Sets 1-5, Revised, ASTM STP-48-J, American Society for Testing Materials, 1960.
21. Sashital, S.R.; and Vedam, K.: Hardening of  $\text{CaF}_2$  Single-Crystal Surfaces Due to Contamination by Atmospheric Oxygen. J. Appl. Phys., vol. 43, no. 11, Nov. 1972, pp. 4396-4400.

TABLE I. - LATTICE PARAMETERS OF POLYCRYSTALLINE COMPOSITIONS IN THE  
BaF<sub>2</sub>-CaF<sub>2</sub> SYSTEM

[Lit. values: BaF<sub>2</sub> = 6.2001 Å (ASTM Card No. 4-0452) (ref. 20);  
CaF<sub>2</sub> = 5.4626 Å (ASTM Card No. 4-0864) (ref. 20).]

BaF <sub>2</sub>	CaF <sub>2</sub>	Melted in Pt crucible in air, Pt/air		Melted in Ni crucible in Ni, Ni/N <sub>2</sub>		Not melted	
Composition, wt %		BaF <sub>2</sub>	CaF <sub>2</sub>	BaF <sub>2</sub>	CaF <sub>2</sub>	BaF <sub>2</sub>	CaF <sub>2</sub>
		Lattice parameters (a <sub>0</sub> , Å) and standard deviation					
100	0	6.202±0.001	(-)	(-)	(-)	6.200±0.001	(-)
90	10	6.195±0.001	a(-)	(-)	(-)	(-)	(-)
80	20	6.192±0.001	a(-)	(-)	(-)	(-)	(-)
70	30	b(-)	a(-)	(-)	(-)	(-)	(-)
62	38	-----	a(-)	6.170±0.001	a(-)	(-)	(-)
60	40	6.190±0.001	a(-)	(-)	(-)	(-)	(-)
50	50	6.192±0.002	a(-)	(-)	(-)	(-)	(-)
0	100	-----	c5.465±0.001	(-)	(-)	(-)	5.471±0.001

aPoor diffraction patterns for CaF<sub>2</sub>, not enough high angle lines for a precision  
lattice parameter determination for these melts.

bPoor XRD pattern.

cTrace CaO.

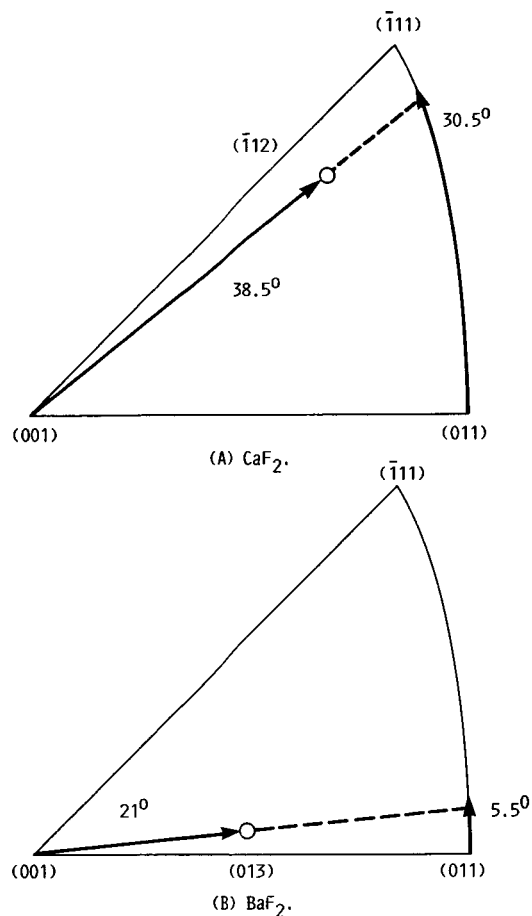


FIGURE 1. - CRYSTAL ORIENTATION OF INDENTATION SURFACE FOR  $\text{CaF}_2$  AND  $\text{BaF}_2$ . THE POINT ON THE UNIT STEREOGRAPHIC TRIANGLE IN THE STANDARD (001) PROJECTION IS THE NORMAL TO THE SINGLE CRYSTAL INDENTATION SURFACE.

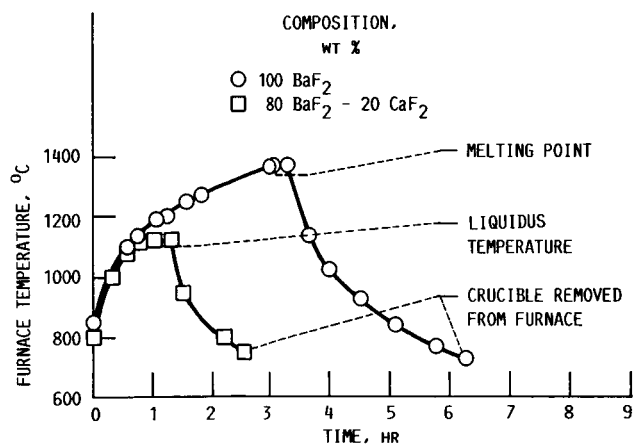


FIGURE 2. - TYPICAL HEATING AND COOLING SCHEDULES FOR MELTING OF  $\text{BaF}_2$  -  $\text{CaF}_2$  BINARY COMPOSITIONS IN PLATINUM CRUCIBLES IN AIR.

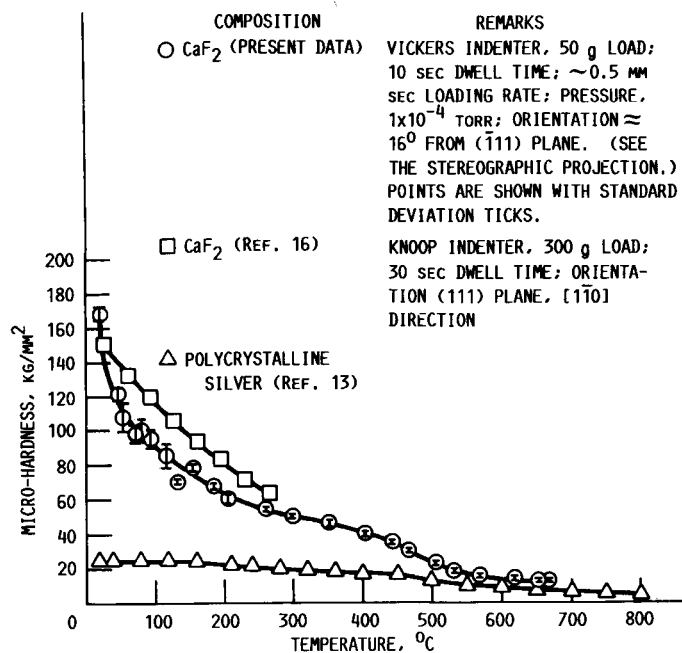


FIGURE 3. - MICRO-HARDNESS OF SINGLE CRYSTAL  $\text{CaF}_2$  AND POLYCRYSTALLINE SILVER AS A FUNCTION OF TEMPERATURE.

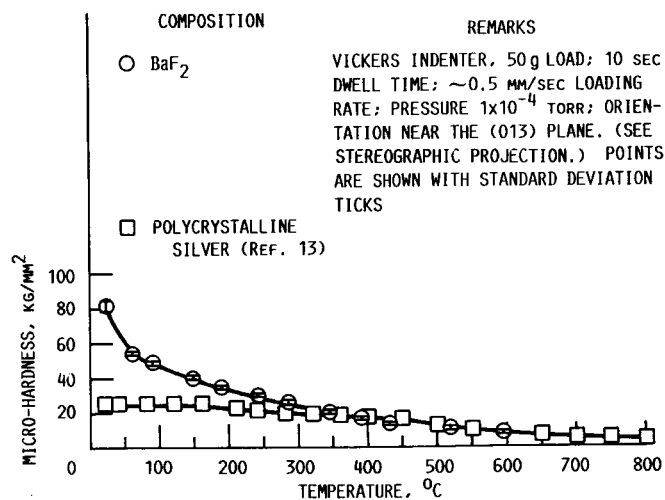


FIGURE 4. - MICRO-HARDNESS OF SINGLE CRYSTAL  $\text{BaF}_2$  AND POLYCRYSTALLINE SILVER AS A FUNCTION OF TEMPERATURE.

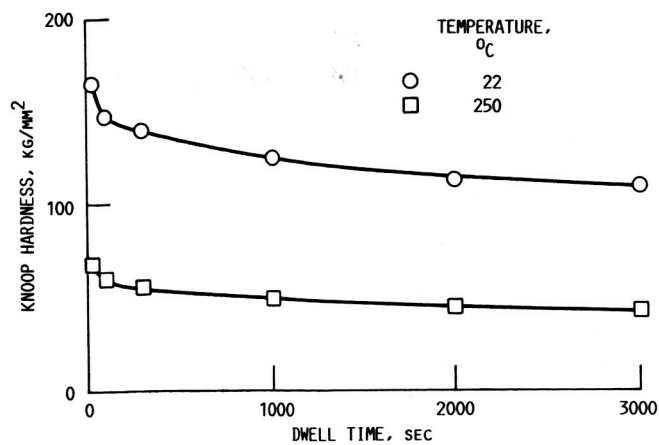


FIGURE 5. - INDENTATION CREEP OF SINGLE CRYSTAL  $\text{CaF}_2$  AT 22 AND 250  $^{\circ}\text{C}$  ON THE  $(1\bar{1}1)$  PLANE AND  $[110]$  CRYSTALLOGRAPHIC DIRECTION (REF. 16).

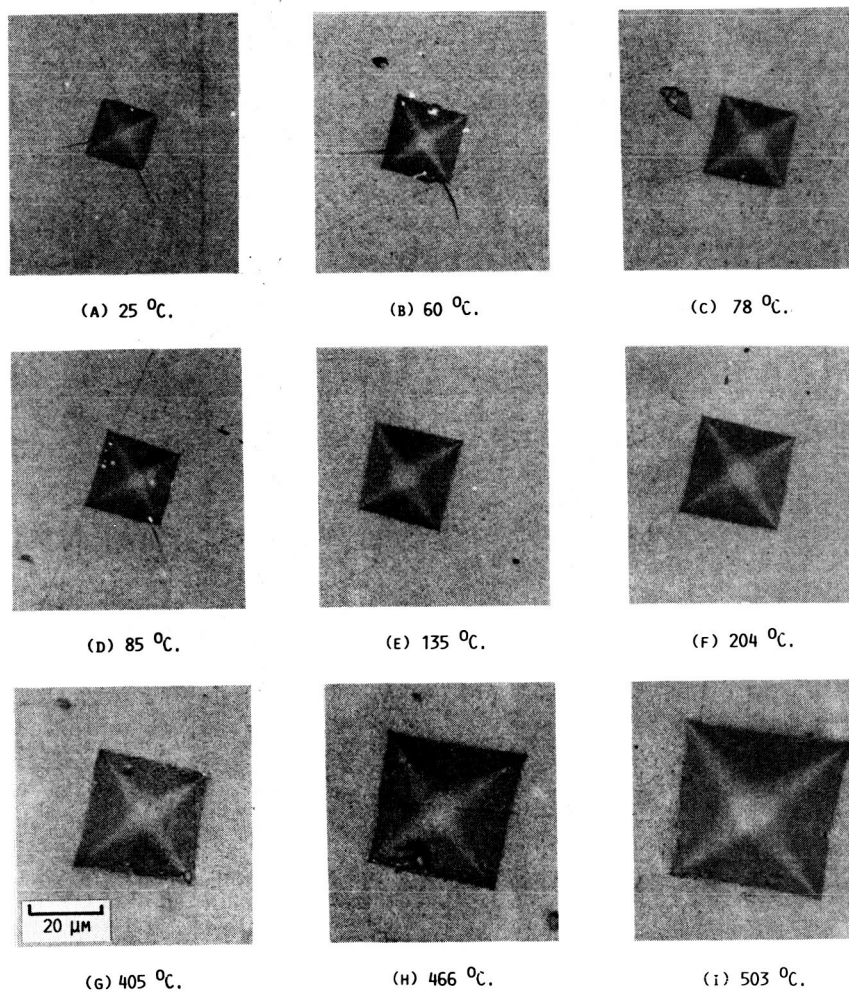
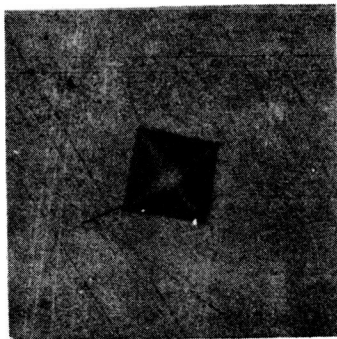
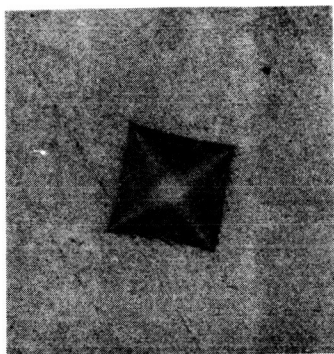


FIGURE 6. - PHOTOGRAPHS OF VICKERS HARDNESS INDENTS OF  $\text{CaF}_2$  SINGLE CRYSTAL AS A FUNCTION OF TEMPERATURE. PHOTOGRAPHS TAKEN AT ROOM TEMPERATURE.

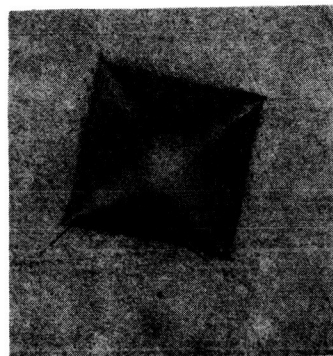
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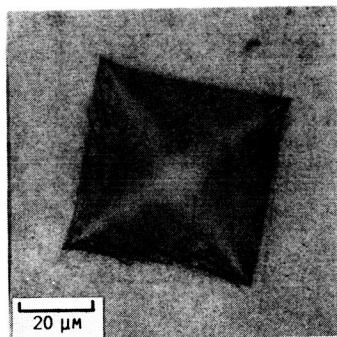
(A) 25 °C.



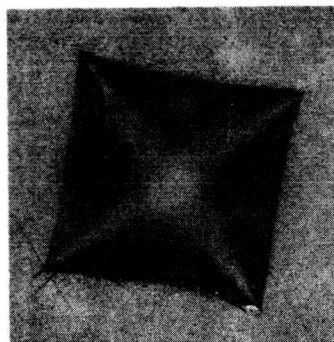
(B) 94 °C.



(C) 289 °C.

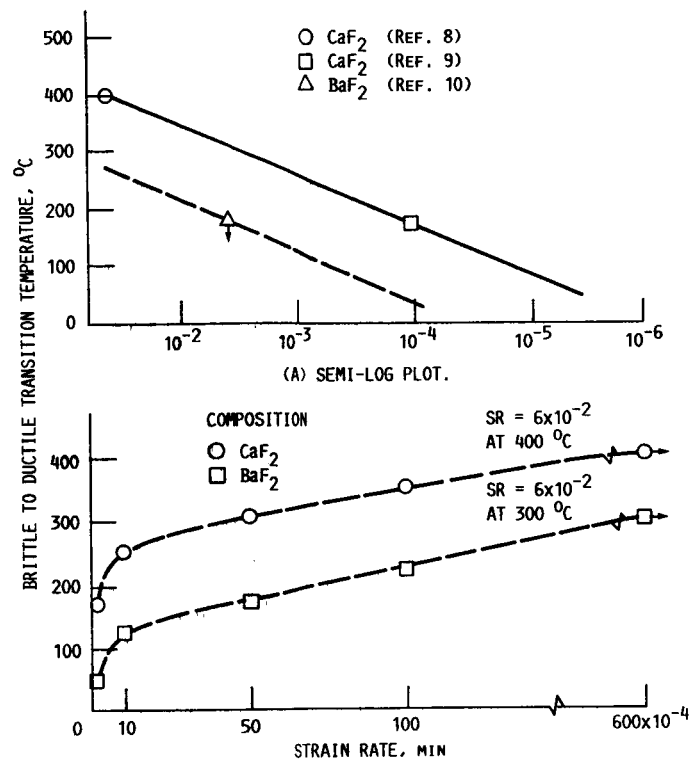


(D) 468 °C.



(E) 520 °C.

FIGURE 7. - PHOTOGRAPHS OF VICKERS HARDNESS INDENTS OF  $\text{BaF}_2$  SINGLE CRYSTAL AS A FUNCTION OF TEMPERATURE. PHOTOGRAPHS TAKEN AT ROOM TEMPERATURE.



(B) DATA FROM FIGURE 8(A) PLOTTED ON A LINEAR SCALE.  
FIGURE 8. - STRAIN RATE VERSUS BRITTLE TO DUCTILE TRANSITION TEMPERATURE FOR SINGLE CRYSTAL  $\text{CaF}_2$  AND  $\text{BaF}_2$ .



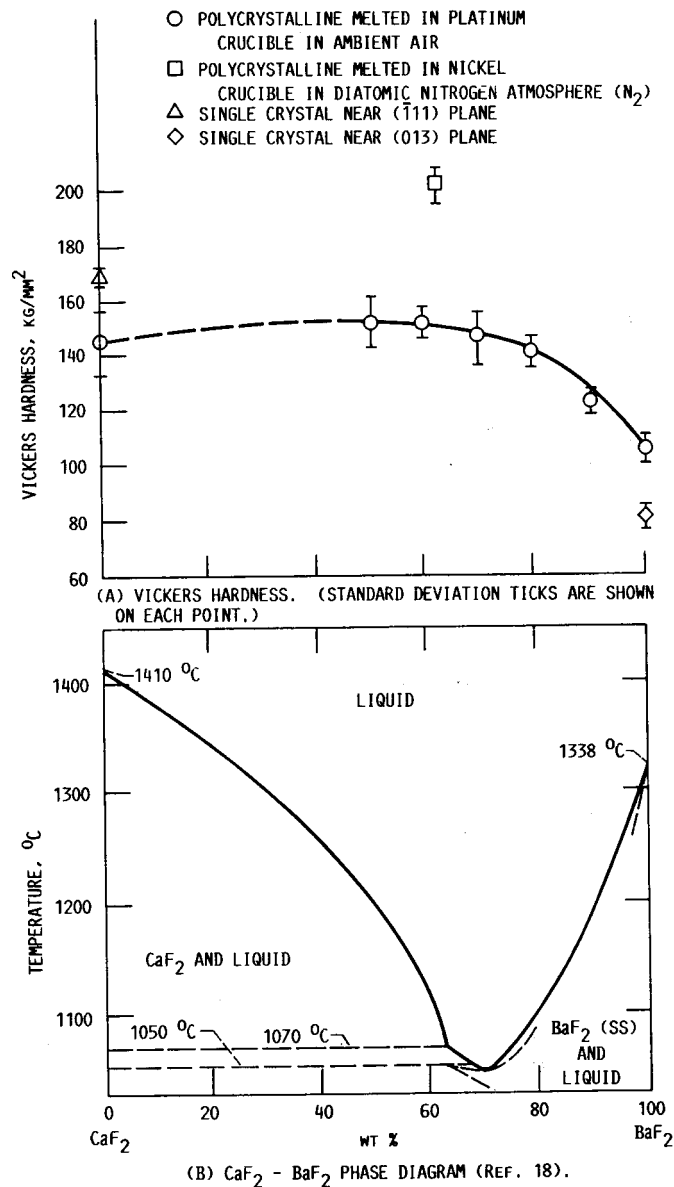


FIGURE 9. -  $CaF_2 - BaF_2$  PHASE DIAGRAM AND VICKERS HARDNESS VALUES AT 25 °C, 50g LOAD.

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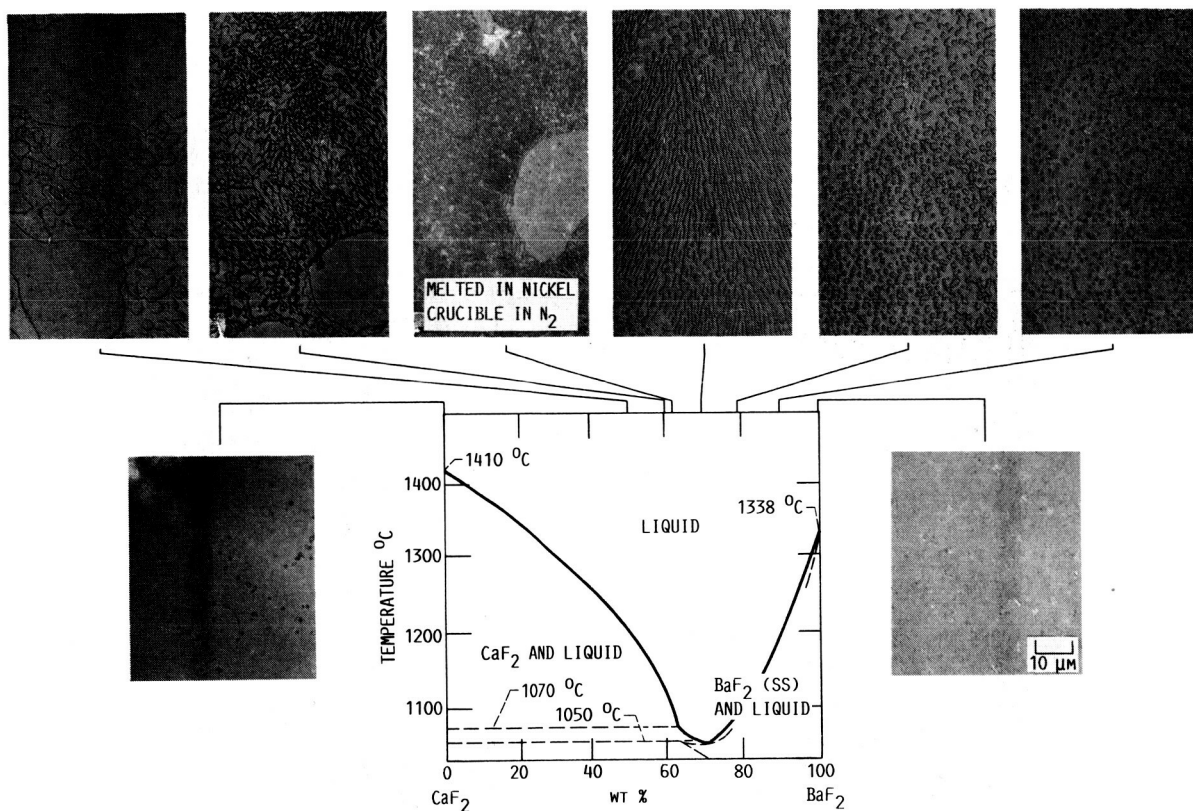


FIGURE 10. - PHOTOMICROGRAPHS OF MELTS IN THE  $\text{CaF}_2$  -  $\text{BaF}_2$  PHASE DIAGRAM (REF. 18). MELTED IN PLATINUM CRUCIBLE IN AIR EXCEPT AS NOTED.

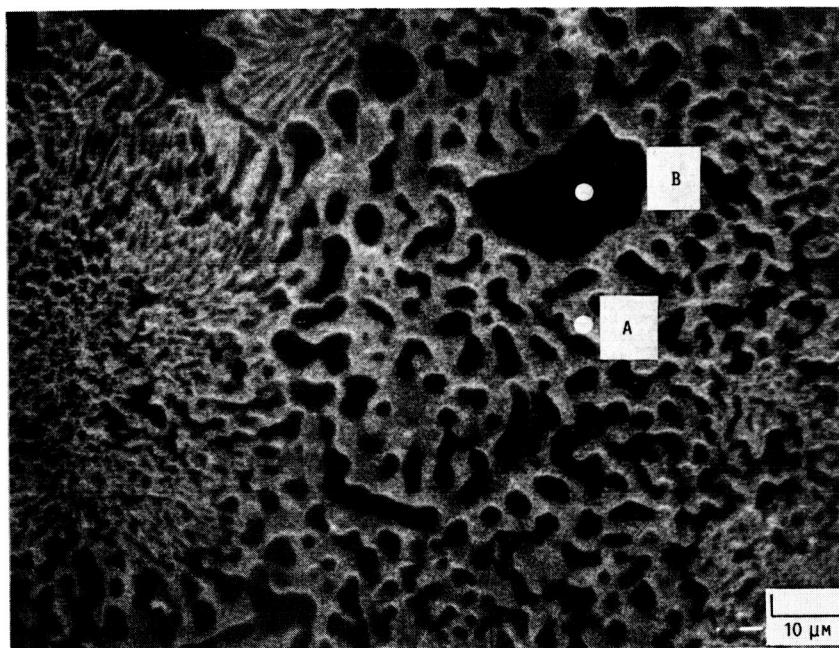
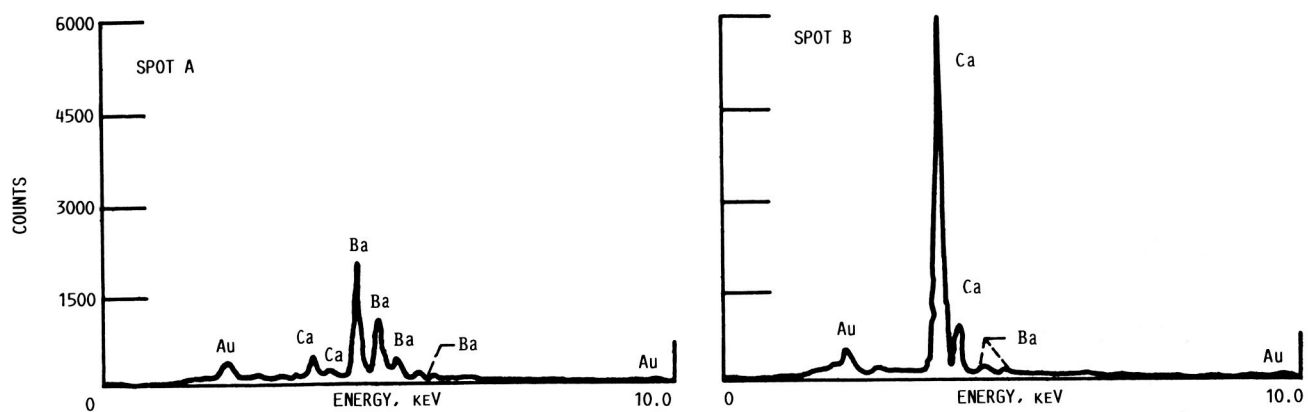


FIGURE 11. - SEM PHOTOGRAPH AND SPOT EDX SPECTRA OF 60 WT %  $\text{BaF}_2$  - 40 WT %  $\text{CaF}_2$  MELTED IN PLATINUM CRUCIBLE IN AIR, POLISHED AND UNETCHED SURFACE. (GOLD COATING FOR SEM EXAMINATION.)

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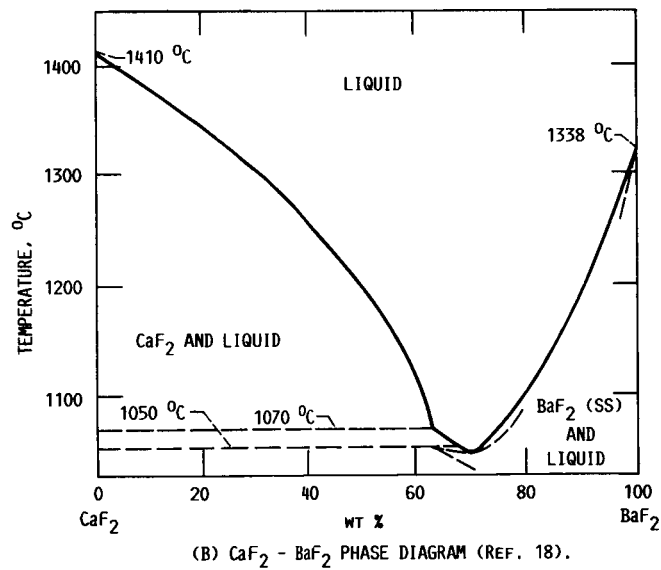
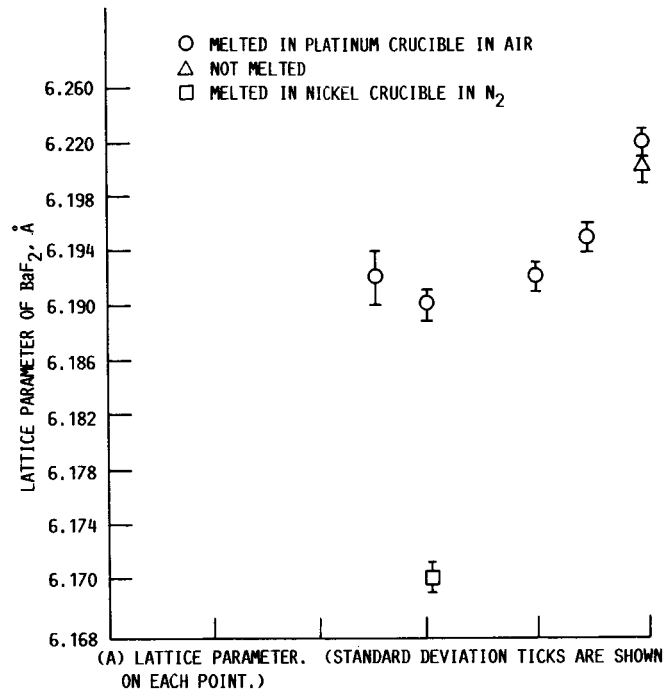


FIGURE 12. - LATTICE PARAMETER OF THE BaF<sub>2</sub> PHASE IN CaF<sub>2</sub> - BaF<sub>2</sub> POLYCRYSTALLINE MELTS.

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16. Abstract  Plastic deformation is a prominent factor in determining the lubricating value of solid lubricants. Little information is available and its direct measurement is difficult so hardness, which is an indirect measure of this property was determined for fluoride solid lubricant compositions. The Vickers hardness of BaF <sub>2</sub> and CaF <sub>2</sub> single crystals was measured up to 670 °C in a vacuum. The orientation of the BaF <sub>2</sub> was near the (013) plane and the CaF <sub>2</sub> was about 16° from the (111) plane. BaF <sub>2</sub> has a hardness of 83 kg/mm <sup>2</sup> at 25 °C and 9 at 600 °C and CaF <sub>2</sub> is 170 at 25 °C and 13 at 670 °C. The decrease in hardness in the temperature range of 25 to 100 °C is very rapid and amounts to 40 percent for both materials. Melts of BaF <sub>2</sub> and CaF <sub>2</sub> were made in a platinum crucible in ambient air with compositions of 50 to 100 wt % BaF <sub>2</sub> . The Vickers hardness of these polycrystalline binary compositions at 25 °C increased with increasing CaF <sub>2</sub> reaching a maximum of 150 kg/mm <sup>2</sup> near the eutectic. The polycrystalline CaF <sub>2</sub> was 15 percent softer than that of the single crystal surface and BaF <sub>2</sub> was 30 percent harder than the single crystal surface. The microstructure of these melts was that of rounded grains of CaF <sub>2</sub> dispersed in a fine BaF <sub>2</sub> matrix. Some small, but undetermined amount of solid solution of CaF <sub>2</sub> in the BaF <sub>2</sub> was found. A melt of 62 wt % BaF <sub>2</sub> -38 wt % CaF <sub>2</sub> was made in a nickel crucible in a nitrogen atmosphere. It was found to be 30 percent harder than the melts made in a platinum crucible in air. It is estimated that the brittle to ductile transition temperature for CaF <sub>2</sub> and BaF <sub>2</sub> is <100 °C for the conditions present in the hardness tester.					
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